

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number
WO 01/46095 A1

(51) International Patent Classification²: C07C 2/12, 9/16

ALLEN, Paul, W. [US/US]; 19407 Point O'woods Court,
Baton Rouge, LA 70809 (US). MATHYS, Georges, M.,
K. [BE/BE]; Eikenboomlaan 66, B-3360 Bierbeek (BE).

(21) International Application Number: PCT/US00/34840
(22) International Filing Date:
20 December 2000 (20.12.2000)

(74) Agents: GRIFFIS, Andrew, B.; ExxonMobil Chemical
Company, P.O. Box 2149, Baytown, TX 77522-2149 et al.
(US).

(25) Filing Language: English

(81) Designated States (national): AU, BR, CA, CN, JP, KR,
MX, SG, US.

(26) Publication Language: English
(30) Priority Data:
9930402.4 23 December 1999 (23.12.1999) GB

(84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(71) Applicant (for all designated States except US): EXXON
CHEMICAL PATENTS INC. [US/US]; 5200 Bayway
Dr., Baytown, TX 77520-5200 (US).

Published:

— With international search report.

(72) Inventors; and

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(75) Inventors/Applicants (for US only): DAKKA, Jihad, M.
[IL/BE]; Heikneuterlaan 7, B-3010 Kessel-Lo (BE). GEE-
LEN, Marc [BE/BE]; Volpestraat 22, B-1500 Halle (BE).



WO 01/46095 A1

(54) Title: PROCESS FOR THE SELECTIVE DIMERISATION OF ISOBUTENE

(57) Abstract: The present invention relates to processes for making a reaction product comprising trimethylpentene(s) which comprises contacting C₄ olefinic feedstock containing isobutene and n-butene(s) with a catalyst comprising zeolite beta under conditions allowing selective dimerization of isobutene to trimethylpentene(s). It also relates to the products obtained by these processes.

PROCESS FOR THE SELECTIVE DIMERISATION OF ISOBUTENE

The present invention relates to selective processes for making a reaction product comprising trimethylpentene(s) from a C₄ olefinic feedstock. It also

5 relates to products obtained by such processes.

Isobutene oligomers are useful intermediates for the preparation of various products of commercial interest, such as isoparaffins, higher alcohols, aldehydes or carboxylic acids having 8, 12 or 16 carbon atoms. Amongst such products, highly branched trimethylpentanes that can be obtained through

10 hydrogenation of trimethylpentenes are of particular interest as gasoline octane number enhancers. Indeed, trimethylpentanes have high RONs (Research Octane Numbers) and MONs (Motor Octane Numbers): 2,2,4-trimethylpentane, also known as iso-octane, has a RON of 100 and a MON of 100; 2,3,4-trimethylpentane has a RON of 109.27 and a MON of 95.9; 2,2,3-trimethylpentane has a RON of 109.9 and a MON of 99.9.

15

One route to produce trimethylpentenes is to dimerise isobutene. However, efficient production of trimethylpentenes from isobutene requires that the process be selective for dimers over oligomers. Oligomerization of isobutene may occur under various acidic conditions using phosphoric acid,

20 trifluoroboron, alumino-silicate or zeolite-containing catalysts. However, such processes usually give mixtures of dimers, trimers, tetramers and higher molecular weight oligomers.

Selective dimerisation of isobutene over trimerisation and higher oligomerisation is known from USP 3,325,465 and DE 3,542,171-A1.

25 In USP 3,325,465, olefinic hydrocarbons having two to six carbon atoms are dimerised to the substantial exclusion of trimers and higher polymers by conducting the polymerisation over aluminosilicates which have been exchanged

with nickel or cobalt ions. Dimerization of isobutene is shown to occur over a 13X molecular sieve which has 95.9 percent of its sodium ions exchanged by cobalt ions with a rate of conversion into dimer over 90 percent, even approaching 100 percent. However, the exact composition of the dimer product 5 is not given. DE 3,542,171-A1 discloses selective dimerisation of isobutene into 2,4,4-trimethylpent-1-ene and -2-ene, using a bismuth and/or lead doped zeolite catalyst at 150 ° C. Selectivity for dimer over trimer formation can be as high as 88 percent.

The processes disclosed in USP 3,325,465 and in DE 3,542,171-A1 are 10 thus selective means for obtaining isobutene dimers from an isobutene feedstock. However, on an industrial scale, it would be more advantageous to use industrial C₄ olefinic feedstocks as obtained from petroleum cracking. Such feedstocks are produced in oil refineries, and usually comprise isobutene, 1-butene and 2-butene; they may also comprise butadiene.

15 A problem associated with the use of isobutene admixed with other C₄ olefins is that isobutene oligomerisation conditions produce codimers of isobutene with the other normal C₄ olefins of the feedstock in addition to the desired isobutene homodimers, i.e. trimethylpentenes. Selective production of trimethylpentenes from a mixed C₄ olefinic feedstock thus requires highly 20 selective process conditions. Catalysts used in such process must not only be selective for dimers over higher oligomers, but they must also favor isobutene homodimerisation over codimerisation of isobutene with the other normal C₄ olefins of the feedstock.

Oligomerisation of isobutene from a mixture of C₄ olefins over zeolite 25 catalysts has been disclosed in USP 4,454,367 and USP 5,091,590.

USP 4,454,367 discloses a method for converting isobutene into low polymers, i.e. a mixture of isobutene dimers, trimers and tetramers, from a C₄ olefinic mixture comprising isobutene and n-butenes. The process uses as catalyst a high silica mordenite having a SiO₂/Al₂O₃ mole ratio of 50 to 200 and advantageously forms low polymers of isobutene. In the examples, a C₄ hydrocarbon mixture consisting of 26.2 mole % of butane, 1.3 mole % of isobutene, 7.5 mole % of 1-butene and 65 mole % of 2-butene was fed into a reactor packed with the high silica mordenite at a temperature of 80 ° C. Under these conditions isobutene conversion rates of up to 93 percent were achieved with low n-butene loss.

USP 5,091,590 discloses a two-stage method for MTBE (methyl tertiary butyl ether) preparation from a C₄ feedstock comprising isobutene, 1-butene and/or 2-butene. In the first stage of the process, the C₄ feedstock is treated with methanol over solid acid etherification catalyst particles (first reaction zone). This produces an intermediate product containing MTBE and unreacted feedstock, including 10-55% unreacted isobutene from the fresh feedstock and excess methanol. The intermediate product is withdrawn from the first reaction zone and fractionated to recover MTBE. The remaining part of the intermediate product then undergoes the second stage of the process; it is contacted with medium pore solid acid catalyst particles to give a product containing MTBE, isobutene oligomer and C5+ alkylate. The preferred catalyst for this second stage is selected from ZSM-5, ZSM-11, ZSM-50, zeolite beta, MCM-22 and mixtures thereof. According to this document, the second stage reaction takes place at 70° to 280°C.

We have now found other process conditions for removing isobutene from industrial C₄ olefinic feedstocks that are selective for trimethylpentenes over other C₈ olefins and higher oligomers.

Accordingly, the present invention provides a process for making a
5 reaction product comprising trimethylpentene(s) which comprises contacting a C₄ olefinic feedstock containing isobutene and n-butene(s) with a catalyst comprising zeolite beta under conditions allowing selective dimerization of isobutene to trimethylpentene(s).

In addition to isobutene, the C₄ olefinic feedstock used in the present
10 process may comprise n-butene, i.e. 1-butene and/or 2-butene. Optionally, these feedstocks may also contain butadiene. Suitable C₄ olefinic feeds include C₄ hydrocarbon mixtures obtained in refining, cracking (catalytic cracking or steam cracking) and/or reforming of oils, butane-butene fractions obtained by removing butadiene from C₄ by-product fractions formed in the production of
15 ethylene by thermal cracking of oils or C₄ hydrocarbon mixtures obtained by dehydrogenation of hydrocarbon mixtures containing n-butane and isobutane.

The present process advantageously oligomerizes isobutene without the need for prior separation of isobutene from the feed. Another advantage of the present process is that it is highly selective for isobutene homooligomerization
20 versus isobutene/n-butene codimerization. Less than 10 wt %, preferably less than 5 wt% of the n-butenes present in the feedstock are oligomerised. Such selectivity is achieved with a catalyst comprising zeolite beta.

For the purposes of the present process, zeolite beta is in proton form, herewith referred to as zeolite H-beta. Zeolite H-beta is a zeolite with relatively
25 large pores. It is available commercially or may be prepared synthetically in different Si/Al atomic ratios ranging for example from 10 to 150. Reference is

made to "Synthesis of High Silica Aluminosilicate Zeolites" by P.A. Jacobs and J.A. Martens (published as volume 33 in the series "Studies in Surface Science and Catalysis") for a review of the synthesis and properties of zeolite beta.

Zeolite beta with Si/Al atomic ratios higher than 150 can be obtained by

- 5 dealumination methods such as hydrothermal (steaming) and/or chemical treatment. We refer to "Introduction to Zeolite Science and Practice", H. Van Bekkum et al., Elsevier 1991, for further details on dealumination. Such dealuminated zeolite H-beta may also be used in the present process.

The zeolite beta catalyst may be used in the form of powders (including
10 powders consisting wholly or in part of single crystals). The zeolite beta catalyst may instead be incorporated in shaped agglomerates, for example, tablets, extrudates or spheres, which may be obtained by combining the zeolite with a binder material that is substantially inert under the conditions employed in the oligomerization process. The zeolite catalyst may be present in amounts from 1
15 to 99% by weight, based on the combined weight of the zeolite and binder material. As binder material there may be used any suitable material, for example silica, metal oxides, or clays, such as montmorillonite, bentonite and kaolin clays, the clays optionally being calcined or modified chemically prior to use. Further examples of such suitable matrix materials include silica-alumina,
20 silica-berylia, silica-magnesia, silica-thoria, silica-titania, silica-alumina-magnesia, silica-alumina-thoria, silica-alumina-zirconia and silica-magnesia-zirconia.

The process according to the present invention may be carried out in various types of reactors suited for heterogenous reactions, either fixed or fluid
25 bed reactors. The process may be carried out in batch or continuous flow reactors or according to the catalytic distillation technique (also called reactive

distillation). Conversion of isobutene from the C₄ olefinic feedstock can take place under liquid, vapor or mixed phases.

The present process selectively converts isobutene present in the C₄ olefinic feedstock into a reaction product comprising trimethylpentenes: dimers 5 represent at least 45 wt %, preferably 60 wt % of all oligomers formed, and trimethylpentenes represent at least 80 wt % of all dimers formed. Such selectivities for trimethylpentenes may be achieved at moderate temperatures, e.g. below 50°C.

Accordingly, the present invention also encompasses the products 10 obtained by contacting a C₄ olefinic feedstock with a catalyst comprising zeolite beta. Said products may be transformed into other products of commercial interest by one or several conversion steps, e.g. fractionation, hydrogenation, hydroformylation followed by oxidation or hydrogenation, carbonylation, etherification, epoxidation or hydration. The present invention also encompasses 15 the products obtained by these further transformation, e.g. alkanes, alcohols, ethers, aldehydes, epoxides or carboxylic acids.

For example, selective dimerization of isobutene from a C₄ olefinic feedstock into a reaction product comprising at least 45 wt % trimethylpentenes, can be immediately followed by hydrogenation. This gives hydrocarbon 20 compositions comprising at least 45 wt % trimethylpentanes, which are useful solvents for cleaning formulations, coating formulations, adhesive formulations and the like.

Dimerization of isobutene from the C₄ olefinic feedstock may be carried out in the presence of an alcohol. In such a case, etherification of 25 trimethylpentenes takes place at the same time as dimerization of isobutene.

The following non-limiting examples illustrate the present invention.

Selective dimerisation of isobutene from an industrial C₄ olefinic feedstock in the presence of various zeolite H-beta catalysts was studied as follows.

The zeolite catalyst (10 wt% of the olefinic feedstock) and C₄ olefinic
5 feedstock (having the following composition, expressed in wt%: 12% isobutane,
19% n-butane, 14% 1-butene, 20.2% isobutene, 20.5% *trans*-2-butene and
13.1% *cis*-2-butene) were loaded into a 1 liter reactor equipped with a heating
element and mechanical stirring. The reactor was pressurized with argon up to
10 bars. The mixture was then heated to 40°C and kept at that temperature for
10 2 hours. After reaction, the reactor was cooled down and sampled under
pressure.

The composition of product mixture was then determined by gas chromatography (GC), using hydrogen as carrier gas. The injector liner was filled with a hydrogenation catalyst (0.03 g of 0.5% Pt on Al) so that, by in-situ
15 hydrogenation, all the components were identified as paraffins. The conversion of butenes/isobutene was determined by comparing the GC analysis of the product mixture with the GC analysis of the feedstock under the same conditions. The feedstock contains butane and isobutane which are inert under the reaction conditions; butane and isobutane were thus used as internal
20 standards for calculating conversion.

The catalysts tested were:

- H-Beta 10 : zeolite H-beta having Si/Al atomic ratio of 10.5, commercially available from Zeolyst International;
- H-Beta 30 : zeolite H-beta having Si/Al atomic ratio of 30, obtained from a
25 zeolite beta in Na form that has been calcined at 550 ° C for 16 hours under air and then exchanged with 0.5 N aqueous NH₄Cl (100 ml solution for 1 g catalyst) under reflux for 12 hours, then dried and calcined at 550 ° C for 10 hours under

- air. The zeolite beta in Na form used in this procedure was prepared synthetically according to the procedure disclosed in EP 187522;
- H-Beta 30 st. : H-Beta described above which has been steamed at 650°C for 16 hours;
- 5 - H-Beta 30 st. reg. : H-Beta 30 st. described above, which has been regenerated after use by drying and calcinating at 550°C for 10 hours under air;
- H-Beta 30 nitric : H-Beta 30 described above, which has been treated with 6N HNO₃ under reflux for 2 hours, filtered and washed until washing liquids were acid free, then dried at 75°C under vacuum overnight;
- 10 - H-Beta 50 : zeolite H-Beta having Si/Al atomic ratio of 50 commercially available from Süd Chemie;
- H-Beta 100 : zeolite H-Beta having Si/Al atomic ratio of 100 commercially available from Süd Chemie;
- H-Beta 150 : zeolite H-beta having Si/Al atomic ratio of 150 commercially
- 15 available from Süd Chemie;
- H-Beta 150 st. : H-beta 150 mentioned above which has been steamed at 650°C for 16 hours;
- H-Beta 150 nitric : H-Beta 150 mentioned above which has been treated with 6N HNO₃ under reflux for 2 hours, filtered and washed until washing liquids
- 20 were acid free, then dried at 75°C under vacuum overnight.

The Table gives the results obtained with each of these zeolites.

In the Table,

- iC4= means isobutene;
- nC4= means n-butene;
- 25 - C8 represents the wt% of dimers formed;
- C12 represents the wt% of trimers formed;
- C16 represents the wt% of tetramers formed;

- NC8 represents the wt% of dimers obtained in the form of octenes (octane after hydrogenation);
 - MC7 represents the wt% of dimers obtained in the form of methylheptenes (methylheptanes after hydrogenation);
- 5 - DMC6 represents the wt% of dimers obtained in the form of dimethylhexenes (dimethylheptanes after hydrogenation);
- TMC5 represents the wt% of dimers obtained in the form of trimethylpentenes (trimethylpentanes after hydrogenation);
 - 2,2,4-TMP represents the portion in wt% of TMC5 in the form of 2,2,4-
- 10 trimethylpentane (after hydrogenation);
- 2,3,4-TMP represents the portion in wt% of TMC5 obtained in the form of 2,3,4-trimethylpentane (after hydrogenation).

Catalyst	Wt(g)	Conversion wt%	Selectivity wt% C8 branchiness (wt%) after hydrogenation									
			iC4=	nC4=	C8	C12	C16	NC8	MC7	DMC6	TMC5	2,2,4 TMP
H-Beta 10	10.0	87	4	60	28	10	0.0	0.0	11	89	45	5
H-Beta 30	10.2	93	6	60	30	8	0.0	0.0	16	84	49	7
H-Beta 30 st.	9.5	50	0	68	24	6	0.0	0.0	3	97	90	3
H-Beta 30 st. reg.	7.5	56	0	71	27	0	0.0	0.0	3	97	91	1
H-Beta 30 nitric	9.4	44	0	74	18	5	0.0	0.0	5	95	82	2
H-Beta 50	6.4	96	7	58	34	7	0.0	0.0	16	84	55	7
H-Beta 100	8.7	100	9	48	33	18	0.0	0.0	19	81	45	8
H-Beta 150	9.1	96	6	55	44	0.0	0.0	0.0	15	85	55	6
H-Beta 150 st.	8.3	32	0	63	27	7	0.0	0.0	7	92	79	3
H-Beta 150 nitric	10.0	53	1	63	35	0.0	0.0	0.0	8	92	74	4

Composition feedstock in wt%, 12% iC4 19% nC4 14% nC4 = 1 20.2% iC4 = 20.5% trC4=2 13.1% cisC4=2

Feedstock is reacted with the catalyst for 2 hrs at 40°C

* Remainder TMP are 2,2,3 and 2,3,3 trimethyl pentane

Claims

1. A process for making a reaction product comprising trimethylpentene(s) which comprises contacting a C₄ olefinic feedstock containing isobutene and n-butene(s) with a catalyst comprising zeolite beta under conditions allowing selective dimerization of isobutene to trimethylpentene(s).
5. 2. A process according to claim 1, characterized in that less than 10 wt % of the n-butene(s) present in the C₄ olefinic feedstock are oligomerized.
3. A process according to claims 1 or 2, characterized in that said zeolite beta 10 has undergone dealumination prior to use.
4. A process according to claim 3, characterized in that dealumination of zeolite beta is performed by steaming and/or chemical treatment.
5. A process according to any of claims 1 to 4, characterized in that it is carried out in a batch or continuous flow reactor.
15. 6. A process according to any of claims 1 to 5, characterized in that it is carried out according to the catalytic distillation technique.
7. A process according to any of claims 1 to 6, characterized in that isobutene dimers represent at least 45 wt %, preferably at least 60 wt % of all products formed, and trimethylpentenes represent at least 80 wt % of all 20 dimers formed.
8. A process according to any of claims 1 to 7, characterized in that the reaction temperature is below 50°C.
9. A process according to any of claims 1 to 8, characterized in that it further comprises anyone or more of the following steps:
25. i) fractionation;
- ii) hydrogenation;
- iii) hydroformylation;

- iv) **oxidation;**
 - v) **carbonylation;**
 - vi) **etherification;**
 - vii) **epoxidation;**
 - 5 viii) **hydration.**
10. A product obtained by the process of claim 9.
11. A hydrocarbon composition comprising at least 45 wt % trimethylpentanes.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/34840

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/12 C07C9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 091 590 A (HARANDI ET AL) 25 February 1992 (1992-02-25) cited in the application claims 5-7	1
A	WO 91 18851 A (EXXON CHEMICAL PATENTS INC) 12 December 1991 (1991-12-12) table VIII	1
X	US 2 276 199 A (L. S. KASSEL) 10 March 1942 (1942-03-10) page 4, left-hand column, line 48 - line 52	9-11
P, X	EP 0 994 088 A (FORTUM OIL & GAS OY) 19 April 2000 (2000-04-19) claims 56-58	9-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

5 March 2001

13/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax (+31-70) 340-3016

Authorized officer

Van Geyt, J

1

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 10 and 11 relate to an extremely large number of possible products. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the products prepared according to the examples.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members				International Application No PCT/US 00/34840	
Patent document cited in search report	Publication date	Patent family member(s)		Publication date	
US 5091590 A	25-02-1992	CA	2041420 A	30-10-1992	
		EP	0639171 A	22-02-1995	
		WO	9313043 A	08-07-1993	
		US	5227534 A	13-07-1993	
WO 9118851 A	12-12-1991	AT	132843 T	15-01-1996	
		CA	2084672 A	08-12-1991	
		DE	69116364 D	22-02-1996	
		DE	69116364 T	11-07-1996	
		EP	0532646 A	24-03-1993	
		ES	2082211 T	16-03-1996	
		US	6008426 A	28-12-1999	
US 2276199 A	10-03-1942	NONE			
EP 0994088 A	19-04-2000	FI	982250 A	17-04-2000	
		AU	6344099 A	08-05-2000	
		WO	0023402 A	27-04-2000	